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SOME FIRST ROW TRANSITION-METAL
COMPLEXES OF PYRROLE-2-ALDEHYDE,
2,2'-(1'-PYRROLINYL)PYRROLE AND
2-(2-PYRIDYL)PYRROLE

CHRISTOPHER L. PERRY

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AND 2-(2-PYRIDYL)PYRROLE

by

CHRISTOPHER L. PERRY

B. S., Rensselaer Polytechnic Institute, 1965

A THESIS

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This Thesis has been examined and approved.

James H. Weber

Robert M. Daenle

Doris W. Ellis

Arthur C. Mathison

August 15, 1969
Date

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Christopher J. Perry

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ABSTRACT

SOME FIRST ROW TRANSITION METAL COMPLEXES OF PYRROLE-2-ALDEHYDE, 2,2'-(1'-PYRROLINYL)PYRROLE AND 2-(2-PYRIDYL)PYRROLE

by

CHRISTOPHER L. PERRY

The following neutral metal ligand complexes have been prepared: The copper(II) and cobalt(III) complexes of pyrrole-2-aldehyde; the zinc(II), copper(II) and nickel(II) complexes of 2,2'-(1'-pyrrolinyl)pyrrole; the zinc(II), copper(II), nickel(II), cobalt(III) and iron(III) complexes of 2-(2-pyridyl)pyrrole; and the cobalt(III) complex of 2-acetylpyrrole. In each case the organic compound acts as a mononegative bidentate ligand. Several of these are new compounds and none has been previously characterized.

The unusual synthetic technique of using boiling xylene, naphthalene or anthracene has been utilized and is shown to be a valuable preparative route for obtaining several of these metal-ligand complexes.

All the complexes prepared were characterized by ultraviolet, visible, and near-infrared spectra; and by magnetic susceptibility. Both solid and solution pyridine adducts of the copper(II) and nickel(II) were investigated. The configurations of the copper(II) and nickel(II) complexes

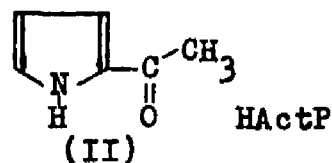
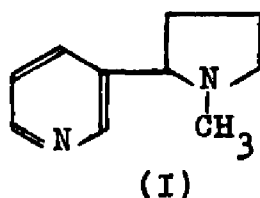
are discussed in light of these measurements.

Proton magnetic resonance spectra were examined for the cobalt(III) and nickel(II) complexes. The anomalous spectrum of the cobalt(III) complex of pyrrole-2-aldehyde is examined in some detail.

INTRODUCTION

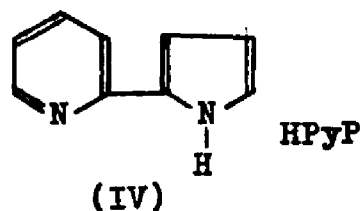
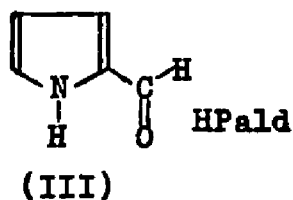
Pyrrole in 1834, and pyridine in 1849, were both first isolated from bone oil.¹ These aromatic nitrogen heterocyclic bases and their many many derivatives have been of increasing interest to chemists ever since.

Many of the derivatives of pyrrole and pyridine are naturally occurring materials. One particularly rich source of aromatic heterocyclic compounds is tobacco, another is coffee. Nicotine (structure I) and a variety of related compounds are found in tobacco. The compound 2-acetylpyrrole (structure II), also named methyl pyrrol-2-yl ketone, and



other pyrrole compounds are found in both coffee and tobacco.

During the 1920's a great deal of work was done in characterizing, identifying and finally synthesizing many of the natural products of tobacco and coffee.²⁻⁶ Three of the products that were investigated are of particular interest to the inorganic chemist. They are: 2-acetylpyrrole (structure II); its precursor pyrrole-2-aldehyde (structure III); and 2-(2-pyridyl)pyrrole (structure IV). These will



hereafter be abbreviated ActP, Pald, and PyP respectively for the anions, and HActP, HPald, and HPyP for the neutral organic compounds.

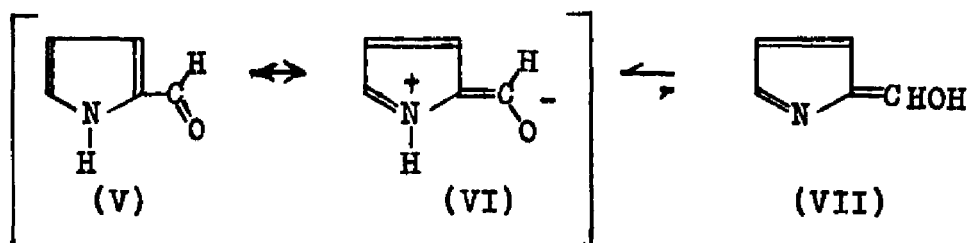
These compounds (structures II, III and IV) in addition to their interesting and important physiological properties, also have the ability to act as bidentate ligands with a number of metals, in particular first row transition series elements. In fact, Emmert and co-workers reported the neutral zinc(II), nickel(II), copper(II), cobalt(III), and iron(III) complexes of PyP, and the copper(II) and cobalt(III) complex of Pald in 1927 and 1929.^{7,8} It appears that none of these complexes has been investigated since.

Emmert prepared these complexes by adding the appropriate metal or metal oxide to a boiling mixture of the organic ligand in either xylene or naphthalene. After recrystallization to obtain pure samples, Emmert's characterization consisted only of elemental analysis, and in a single case, a melting point.⁷

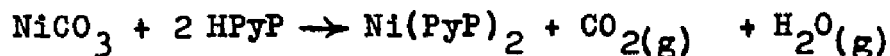
The synthetic technique of boiling a metal source with a ligand in a high boiling solvent such as naphthalene to obtain the metal complex has not been common in modern times. While such a method may not be a standard synthetic technique for the inorganic chemist, it is evident from the present investigation that the inorganic chemist should not completely discount such a procedure. With the variation of using metal carbonates as the metal source when possible,

a simple and rapid preparation of a number of complexes has been effected. Probably the only definite restriction for using such a method is that both the ligand and the resulting complex must be fairly stable at the high temperature being employed.

The thermal stability of HPyP is not surprising in view of the high degree of conjugation of the molecule. HPald and HActP at first appraisal would not be expected to be so stable. The stability of HPald has interested chemists for many years and has been well investigated.^{9,10} It is felt that the stability is due to resonance (structures V and VI), and that it may also be contributed to by the tautomeric alcohol form (structure VII).

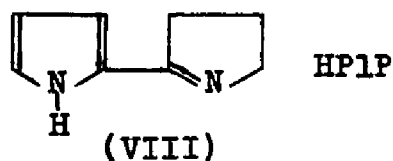


Using nickel(II) carbonate and HPyP as examples, an illustrative reaction may be written as:



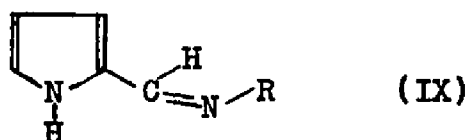
This is in no way an attempt to specify the mechanism of the reaction, but merely to designate the probable stoichiometry. In any event, the resulting compounds are stable, neutral, metal-organic complexes; soluble in organic solvents.

Three complexes of 2,2'-(1'-pyrrolinyl)pyrrole (structure VIII), which will hereafter be abbreviated PlP



for the anionic ligand and HPlP for the neutral organic molecule, were also prepared. This derivative of bipyrrole has been prepared by Rapoport *et al.*¹¹ and subsequent investigators.¹² However, metal complexes of PlP have not been previously reported.

Inorganic complexes of pyrrole derivatives have been investigated in recent years by several authors. A number of N-R-pyrrole-2-aldeimino (structure IX) chelate

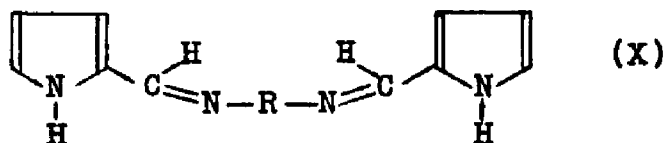


complexes have been prepared by Holm and co-workers,^{13,14} Chakavorty¹⁵⁻¹⁷ and others.¹⁸ The R substituent has been a wide variety of molecules from hydrogen and simple alkyl to branched alkyl and aryl groups.

Several of the nickel(II) complexes have been shown by spectral, magnetic and nuclear magnetic resonance measurements to have a tetrahedral-planar equilibrium in solution.¹⁴ A number of cobalt(III) complexes were investigated by

proton resonance techniques and shown to be in a trans configuration.^{13,17} The ultraviolet-visible absorption spectrum was also examined for these compounds,¹⁵ as well for several copper(II) complexes.^{14,16,18} In addition a few palladium(II), zinc(II) and mercury(II) complexes have been studied.^{14,18}

Weber has prepared a number of copper(II) and nickel(II) complexes with tetradentate pyrrole derivative ligands (structure X), where R was a variety of alkyl and



aryl groups.^{19,20} Weber concluded that the nickel(II) complexes were square-planar, and that the copper(II) complexes were planar or pseudo tetrahedral. In addition to ligand field and magnetic measurements, the complexes were also characterized by infrared and ultraviolet spectral properties.

Pyrrole derivative ligand-metal complexes have been of considerable interest since such complexes can be viewed as analogs or proto-types of important biological systems. Naturally occurring pyrrole-derivative ligand-metal complexes such as porphyrins, phthalocyanines and dipyrromethenes play key roles in many life systems.²¹ Thus it is not improbable that newly synthesized pyrrole derivative

complexes could in the future be found to have important medicinal properties.

During the past few decades the field of coordination chemistry has come into its own right. Ligand field theory, crystal field theory, molecular orbital theory and others have been developed, tested and refined. The triumph lies in the fact that one can frequently obtain valuable insight into the atomic and molecular structure of complexes by studying such physical properties as absorption spectra, magnetic moment, and others. The present work may be viewed as being a contribution to the continuing effort to understand the interaction of molecules and metals in coordinated complexes.

EXPERIMENTAL

Materials.--The ligand pyrrole-2-aldehyde, also named pyrrole-2-carboxaldehyde, was purchased from Aldrich Chemical Company and was recrystallized from low boiling (30-50°) petroleum ether before use. The compound 2-acetylpyrrole, also named methyl pyrrol-2-yl ketone, was purchased from Eastman Organic Chemicals and used without further purification. Other chemicals used are readily available.

The metal sources were generally reagent grade quality, except for the materials referred to hereafter as the "basic carbonates" of copper, nickel and cobalt. These materials were prepared by treating an aqueous metal(II) chloride solution with an excess of sodium carbonate solution. The resulting precipitate was washed with distilled water until a negative chloride test was obtained, then collected, dried, and ground to a fine powder. The products, which react with acid to release carbon dioxide, were not further characterized and were used as the metal source for several of the complex preparations.

All solvents were dried by standard techniques²² and were stored over 4A molecular sieves or sodium wire. Special precautions were taken with tetrahydrofuran (THF) to avoid dangerous peroxide formation.²³ Materials which were used as the reaction media for several of the preparations reported have the following melting and boiling points:²⁴

<u>Compound</u>	<u>mp. °</u>	<u>bp. °</u>
Xylene	<0	138-139
Naphthalene	80.2	217.9
Anthracene	217	354-355

Preparation of 2,2'-(1'-Pyrrolinyl)pyrrole.--The ligand HPlP was prepared from pyrrole and 2-pyrrolidine with phosphorus oxychloride using the procedure detailed by Rapoport and Castagnoli.¹¹ After the reaction is complete the mixture must be made basic to a pH of 10. It is, however, necessary to recheck the pH after 20 to 30 min since there is a tendency for the reaction to revert to an acidic solution due to the hydrolysis of the phosphorus oxychloride. If a pH of 10 is not maintained a poor yield will result.

Preparation of 2-(2-pyridyl)pyrrole.--To obtain the ligand HPyP the intermediate N-(2-pyridyl)pyrrole was prepared by a variation of the method of Emmert et al.⁷ This consisted of using xylene as a solvent for the reaction between potassium pyrrole and 2-chloropyridine, in a 1:1 mole ratio. The reaction mixture was refluxed for 30 hr, and the product was vacuum distilled.

When 2-chloropyridine was used as a starting material, a 60% yield was obtained. When 2-bromopyridine was used, only a 47% yield was obtained.

The thermal rearrangement of N-(2-pyridyl)pyrrole to

2-(2-pyridyl)pyrrole was accomplished using the method of Wibaut et al.² This consisted of distilling the N-(2-pyridyl)-pyrrole through a quartz tube packed with 4 mm Berl saddles. The 10-mm tube was heated to $700 \pm 10^\circ$ over a length of 50 cm. A stream of nitrogen was run through the apparatus during the distillation. (See Figure I.)

Approximately 85 g of N-(2-pyridyl)pyrrole was used in the rearrangement reaction, and 80.1 g of crude product was collected. The crude product was subjected to steam distillation. From the first 2 l. of distillate an oil was collected, and the next 4 to 5 l. of distillate yielded a white solid. The oil was vacuum distilled and shown to be largely unrearranged N-(2-pyridyl)pyrrole by formation of the picrate derivative which had a mp range of $141-143^\circ$. Wibaut gives the mp as 143° .² The white solid which was collected and dried had a weight of 32.4 g for a yield of 38%. The picrate derivative of the solid, recrystallized from ethanol, had a mp of 223° . Wibaut gives the mp of the picrate of 2-(2-pyridyl)pyrrole as $222.5-223.0^\circ$.^{2,5} In addition, 7 g of 3-(2-pyridyl)pyrrole was recovered from the distillation flask by extraction with hot water.

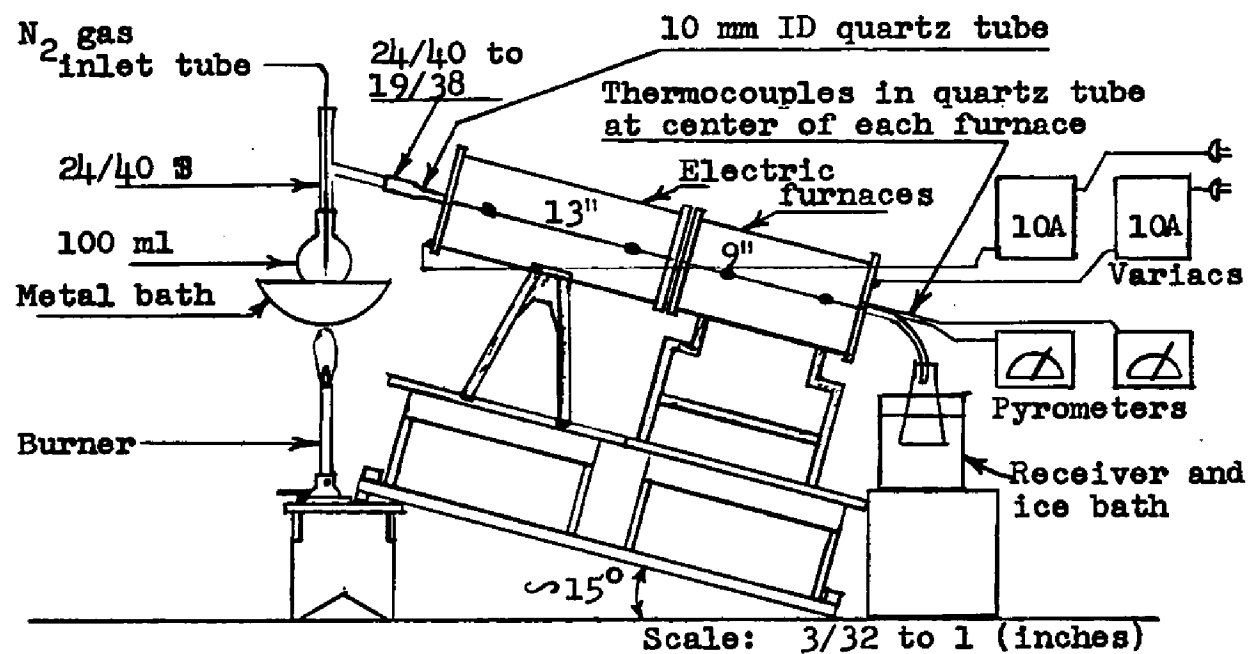
Preparation of Cu(Pald)_2 .--This complex was made by a modification of the method of Emmert et al.⁸ substituted for the "precipitated copper oxide" of Emmert's method was the basic carbonate of copper(II). One gram of this source and 1 g of HPald ligand were placed together

in a 3/4 x 10 inch reaction tube with 3 to 4 ml of xylene; the metal source was thus in excess. The mixture was refluxed for 20 min. The xylene was then filtered hot with the aid of a few ml of chloroform. On cooling, dark green needle-like crystals were formed. The dried crystals weighed 1.0 g for a yield of 75% based on the amount of HPald used. The complex was recrystallized in 50 ml of 1,2-dichloroethane, yielding dark green needles having a mp range of 183-185° with decomposition.

Preparation of Co(Pald)₃.--This complex was prepared by a modification of the method of Emmert et al.⁸ Substituted for the "cobalt oxide" of Emmert's method was the basic carbonate of cobalt(II). One gram of this cobalt source, which is an excess of metal, and one gram of HPald ligand were placed in a 50-ml flask with 20 ml of xylene. The flask was fitted with a condenser and a gas inlet tube so that a stream of air could be bubbled through the reaction mixture as it refluxed. After 8 hr of refluxing the reaction mixture was filtered, the xylene removed on a rotary evaporator, and a fair amount of unreacted HPald removed by sublimation. The crude product weighed 0.26 g for a yield of 22%. The complex was recrystallized from absolute ethanol yielding fine red needles having a mp range of 201-203°.

The complex can also be prepared in THF from anhydrous cobalt(II) chloride, potassium t-butoxide and HPald by Holm's method.¹³ Using this method, anhydrous cobalt(II) chloride

Figure I



Apparatus for the Preparation of 2-(2-Pyridyl)pyrrole

was added to the slurry formed by the addition of potassium t-butoxide to a solution of HPald in dry THF. The mixture was then stirred for 48 hr and the THF filtered off. A second portion of THF was added to the solid and stirred for an hour, filtered off and added to the original portion of THF. The THF was removed on a rotary evaporator and the remaining oil vacuum dried for several hours or a day. The solid residue in the flask was then washed with two small portions of absolute ethanol, which were discarded. The remaining light brown powder was then dissolved in the necessary amount of warm absolute ethanol and filtered; with cooling, a mass of very fine crystals separated. Some ethanol was removed and a second crop obtained. A yield of about 25% of the purified product was obtained from this reaction.

Preparation of $\text{Co}(\text{ActP})_3$.--This compound was prepared by placing 1 g of HActP ligand in a 3/4 x 10 inch reaction tube with 2-3 g of naphthalene and heating to a low boil. The tube was left open to the air throughout the reaction. Added slowly to the boiling mixture was 1 g of the basic carbonate of cobalt(II). Heating was continued for 10 min. After dissolving in chloroform, the reaction product was filtered, the chloroform removed by rotary evaporation and the naphthalene and excess ligand removed by sublimation in a vacuum desiccator at 60°. The residue was dissolved in a minimum of absolute ethanol, filtered and

allowed to cool. The resulting mass of dark red crystals was separated and dried. A yield of about 45% was obtained. The complex has a mp range of 200-202°.

Preparation of Zn(PlP)_2 .--This complex could not be prepared in xylene or naphthalene. It was prepared using boiling anthracene in the following manner. To 1 g of HPlP in 2 g of recrystallized anthracene in a 3/4 x 10 inch reaction tube, 1 g of anhydrous zinc carbonate was added over a period of 5 min while the anthracene was kept at a low boil. Heating was continued for an additional 5 min. The brownish mass was filtered with the aid of benzene, and the benzene was removed using a rotary evaporator. The anthracene was removed in a heated vacuum desiccator by sublimation at 100° over a period of three days. The remaining brown powder was recrystallized three times from dry benzene to give approximately 0.4 g of light tan (nearly white) crystals for a yield of 32%. The complex has a mp range of 273-275°.

Preparation of Cu(PlP)_2 .--At room temperature a solution of 1.067 g of HPlP (0.008 mol) in 40 ml of methanol was added dropwise over a period of 6 or 7 min to a solution of 0.799 g of copper(II) acetate monohydrate (0.004 mol) in 50 ml of 80% aqueous methanol. Upon addition of the ligand solution a purplish-tan precipitate was formed. The reaction mixture was stirred for five minutes after the ligand addition was complete and was filtered. To the filtrate was added 15

ml of 0.3 M sodium carbonate, and an additional small portion of precipitate was collected. The dry combined weight of the precipitates was 1.25 g, for a yield of 97%. The complex was recrystallized from 50 ml of 1,2-dichloroethane to give fine light-purple needles, having a mp range of 227-228°.

Preparation of $\text{Ni}(\text{PlP})_2$.--At room temperature a solution of 1.560 g of HP1P (0.012 mol) in 40 ml of 95% ethanol was added dropwise over a period of 10 min with stirring to a solution of 1.496 g of nickel(II) acetate tetrahydrate (0.006 mol) in 100 ml of 75% aqueous ethanol. After a few ml of ligand solution had been added, an orange precipitate appeared. The reaction mixture was stirred for 5 min after completion of the ligand addition and was filtered. Twenty ml of 0.3 M aqueous sodium carbonate was added to the filtrate and a small additional amount of orange precipitate was obtained. The combined precipitates were thoroughly dried and had a combined weight of 1.46 g for a yield of 75%. The complex was recrystallized from 200 ml of 1,2-dichloroethane to give very fine orange crystals having a mp range of 309-311° with decomposition. The complex is nearly insoluble in most solvents, exhibiting its greatest solubility in chlorinated solvents.

Preparation of $\text{Zn}(\text{PyP})_2$.--This complex was prepared by the method of Emmert et al.⁷ The method consisted of adding 1 g of zinc oxide in portions to a boiling mixture of 1 g of HPyP ligand and 2 g of naphthalene. Heating was

continued for 30 min. After dissolving the reaction product in benzene, the yellow-brown solution was filtered, the benzene removed by evaporation and the naphthalene removed by sublimation in a vacuum desiccator at 60° . The residue was recrystallized twice from benzene to give 0.44 g of bright yellow crystals for a yield of 38%. The yellow crystals have a mp range of $264-266^{\circ}$.

Preparation of $\text{Cu}(\text{PyP})_2$.--This complex was prepared by the method of Emmert et al.⁷ The method consisted of adding a cold solution of 1.15 g of HPyP (0.008 mol) in 25 ml of 95% ethanol to an ice-cold solution of ammoniacal copper(II) sulfate. The copper solution was prepared from 1.09 g of copper(II) sulfate pentahydrate (0.0044 mol) in 25 ml of water to which 15 M ammonia had been added until a clear blue solution was obtained. Upon addition of the ligand solution, a thick green precipitate appeared. The precipitate was collected and washed with a cold solution of 200 ml of 3 M ammonia to remove any traces of excess copper sulfate. After thorough vacuum drying the precipitate was dissolved in 250 ml of hot high boiling ($95-110^{\circ}$) petroleum ether. The dark green solution was filtered while hot and cooled slowly. After several hours, 0.87 g of dark green needle-like crystals were obtained for a yield of 62%. The material has a mp range of $148-150^{\circ}$. (Lit.⁷ $149-151^{\circ}$).

Preparation of $\text{Ni}(\text{PyP})_2$.--This complex was prepared

using a variation of the method of Emmert et al.⁷ The preparation consisted of placing 1 g of HPyP ligand in a 3/4 x 10 inch reaction tube with 2-3 g of naphthalene and heating to a low boil. Heating was continued for 20 min while 1 g of the basic carbonate of nickel(II) was slowly added to the boiling mixture. After dissolving the reaction product in chloroform the solution was filtered, the chloroform removed by rotary evaporation and the naphthalene removed by sublimation in a vacuum desiccator at 60°. The residue was dissolved in 150 ml of a solution of four parts high boiling (95-115°) petroleum ether and five parts benzene. The solution was filtered while hot and slowly cooled while benzene was vacuum evaporated in a desiccator. From the solution 0.82 g of product was collected as dark purple-brown flakes for a yield of 70%. The crystals gave a mp range of 176-178°.

Preparation of Co(PyP)₃.--This compound was prepared by a slight variation of the method of Emmert et al.⁷ The procedure was the same as that described for Ni(PyP)₂. In this case 1 g of the basic carbonate of cobalt(II) and 1 g of HPyP were used. The reaction was left exposed to the air. The complex was recrystallized from 120 ml of benzene to which 50 ml of high boiling (95-110°) petroleum ether had been added. From the solution 0.67 g of a crystalline orange powder was obtained, for a yield of 60%. The complex has a mp range of 373-375°.

Preparation of Fe(PyP)_3 .--This complex was prepared by the method of Emmert *et al.*⁷ using 1 g of fine iron powder with 1 g of HPyP. Other than the metal source, the procedure was the same as that for Ni(PyP)_2 . The complex was recrystallized from 50 ml of benzene to which 150 ml of low-boiling ($30-50^\circ$) petroleum ether had been added. In solution the complex is extremely dark red and the dry crystalline product is lustrous black flakes. Obtained was 0.22 g of material for a yield of 20%. The complex has a mp range of $274-275^\circ$.

Preparation of Adducts with Pyridine.--When the copper and nickel complexes were dissolved in pyridine, all exhibited a distinct color change. The copper complexes formed green solutions and the nickel complexes gave pale yellow solutions. The other complexes prepared showed no change by being dissolved in pyridine. The solid adducts of the copper and nickel complexes were formed by allowing freshly ground samples to stand in an atmosphere of pyridine for 24 hr.

For Cu(PlP)_2 , which does not form an adduct in this manner, recrystallization from pyridine was attempted. From the dark green pyridine solution only the purplish-tan crystals of Cu(PlP)_2 could be obtained. The pyridine- Cu(PlP)_2 adduct which appears to exist in solution has not been prepared as a solid. (See Table III.)

Elemental Analyses.--Nitrogen analyses were performed with a Coleman Model 29 Nitrogen Analyzer. Other analyses

were performed by the Galbraith Microanalytical Laboratories and at the University of New Hampshire with a F&M Model 185 CHN Analyzer. (See Table I.)

Analysis of Pyridine Adducts.--In order to determine the amount of pyridine added by the nickel and copper complexes the change in weight of the complexes was measured. Careful weighings were made before and after freshly ground samples of the solid complexes were exposed to an atmosphere of pyridine. The added pyridine was removed in a vacuum desiccator at 40° and the original complexes were recovered. Duplicate determinations were made for each complex.

Ultraviolet, Visible and Near-Infrared Spectra.--In all cases the ultraviolet, visible and near-infrared spectra were obtained at room temperature using a Cary 14 recording spectrophotometer. For the complexes "Fisher Spectranalyzed Reagent" 1,2-dichloroethane was used as the solvent, except for Zn(PyP)_2 which decomposes in this solvent. In this case reagent grade toluene was used as the solvent. Solutions were made to approximately 10^{-2} M. Dilutions for lower concentrations were made using a Gilmont Model 7876 precision micrometer buret. The ultraviolet region was generally run at approximately 5×10^{-5} M in matched 1-cm silica cells. The ligand field regions usually required concentrations from 10^{-2} to 10^{-3} M. In each case, concentrations were adjusted for duplicate runs so that bands appeared having an absorbance (A) of between 0.2 to

Table I

Melting point, Magnetic, and Analytical data of the Complexes Prepared

<u>Complex</u> ^a	<u>Color</u> ^a	<u>Mp Range</u> ^b	<u>μ_{eff}</u> ^c	<u>Calculated %</u>			<u>Found %</u>		
				<u>C</u>	<u>H</u>	<u>N</u>	<u>C</u>	<u>H</u>	<u>N</u>
Cu(Pald) ₂	green	201-203	1.87	47.71	3.20	11.13	47.93	3.23	11.24
Co(Pald) ₃	red	183-185	0.44 ^d	52.80	3.55	12.32	52.75	3.52	12.45
Co(ActP) ₃	dark red	200-202	Dia. ^d	56.40	4.73	10.96	56.42	4.70	10.88
Zn(PlP) ₂	v. lt. brown	273-275	-	57.93	5.47	16.89	57.81	5.46	16.89
Cu(PlP) ₂	purple-tan	227-228	1.86	58.25	5.50	16.98	58.22	5.37	16.91
Ni(PlP) ₂	orange red	309-311	0.45 ^d	59.12	5.58	17.24	59.40	5.53	17.02
Zn(PyP) ₂	yellow	264-266	-	61.47	4.01	15.93	61.85	3.93	15.71
Cu(PyP) ₂	dark green	149-151	1.85	61.79	4.03	16.01	61.59	4.07	16.24
Ni(PyP) ₂	dk. red-brown	176-178	0.46 ^d	62.66	4.09	16.24	62.43	3.99	16.19
Co(PyP) ₃	orange red	373-375	0.56 ^d	66.39	4.33	17.21	66.44	4.30	17.14
Fe(PyP) ₃	v. dk. purple	274-275	2.26	66.81	4.36	17.31	67.08	4.58	17.09

a. Abbreviations: Pald, pyrrole-2-aldehyde; PlP, 2,2'-(1'-pyrrolinyl)pyrrole; PyP, 2-(2-pyridyl)pyrrole; v., very; lt., light; dk., dark.

b. Uncorrected, °C

c. Average value in BM measured at room temperature at 5.8 and 8.6 kgauss

d. Diamagnetic in deuteriochloroform by nuclear magnetic resonance

0.8 Due to the low solubility of Ni(PlP)_2 , 10-cm Beckman near-infrared silica cells had to be used for the ligand field region of this compound. The spectrum of each complex was examined up to 2000 $\text{m}\mu$ and all complexes were examined in at least independent duplicate runs. (See Table II.)

For the pyridine adducts of the copper and nickel complexes the ultraviolet, visible and near-infrared spectra were recorded with the complexes dissolved in "Fisher Certified ACS" grade pyridine. As before, concentrations were adjusted on subsequent runs of each complex to bring the absorbance (A) of bands to between 0.2 and 0.8. The 1-cm silica cells were used except for Ni(PlP)_2 for which the 10-cm cells had to be used. The molar extinction coefficients ϵ , having the units $\text{l. mol}^{-1} \text{ cm}^{-1}$, reported are based on the amount of complex initially dissolved in the pyridine. The spectrum of each complex was examined up to 1300 $\text{m}\mu$. (See table III.)

Infrared Spectra.--All measurements were made at room temperature on a Beckman IR-12 infrared spectrophotometer. The ligands and complexes were studied as solids in Nujol and halocarbon mulls. In the region 200 cm^{-1} to 600 cm^{-1} polyethylene plates were used for the Nujol mulls. At higher frequency sodium chloride and cesium iodide plates were satisfactory. The instrument was calibrated against atmospheric water vapor and carbon dioxide in the single beam mode.

Table II

The Ultraviolet, Visible and Near-Infrared Spectra of the Complexes Prepared^a

<u>Compounds</u>	<u>Ligand Field, cm⁻¹ b</u>	<u>Ultraviolet, mμ, (e x 10⁻⁴)^b</u>			
HPald		253(0.50)	287(1.71)		
Cu(Pald) ₂	15,870 (61) br	254(1.26)	287(3.36)	328(0.446) sh	
Co(Pald) ₃	18,900 (128)	302(1.81)	346(1.95)		
HP1P		276(0.69)	322(1.70)		
Zn(P1P) ₂	26,110 (13)	250(0.78) sh	305(2.73)		
Cu(P1P) ₂	20,660 (179)	263(1.38)	320(2.23)	390(0.112) sh	
Ni(P1P) ₂	21,050 (169) br	304(1.90)	319(0.174)	391(0.446) sh	406(0.415) sh
HPyP		292(1.36) sh	312(1.64)		
Zn(PyP) ₂		325(3.32)	378(1.88)		
Cu(PyP) ₂	18,250 (317) br	292(1.85) sh	312(2.21)	276(1.18)	
Ni(PyP) ₂		291(2.39)	313(2.79)	368(.77)	393(.68) sh
Co(PyP) ₃		279(1.63)	322(2.96)	375(2.54)	
Fe(PyP) ₃	15,625-13,160 (415)	316(3.66)	361(2.47)	530(0.301)	

a. Abbreviations: Pald, pyrrole-2-aldehyde; P1P, 2,2'-(1'-pyrrolinyl)pyrrole; PyP, 2-(2-pyridyl)pyrrole; br., broad; sh., shoulder

b. Molar extinction coefficients, e, in parentheses, are in l. mol⁻¹cm⁻¹

Table III

Copper(II) and Nickel(II) Adducts With Pyridine

<u>Complex^a</u>	<u>Solid Ratio^b</u>	<u>Color (Solid)</u>	<u>Color (Solution)^c</u>	<u>Ligand Field (cm⁻¹)^{c,d}</u>	<u>Ultraviolet (mμ)^{c,d}</u>
Cu(Pald) ₂	2.00	dark green	blue-green	16,860(74.0)	328(5.92x10 ³)
Cu(PlP) ₂	0.00	purple-tan	yellow-green	15,720(88.1)	328(1.93x10 ⁴) 392(3.87x10 ²) sh 447(1.86x10 ²) sh
Cu(PyP) ₂	1.05	dark green	blue-green	18,800(105) 14,970(186) 13,180(167) sh	320(2.34x10 ⁴) 368(1.03x10 ⁴)
Ni(PlP) ₂	1.98	pale blue	pale yellow	17,950(9.24) 10,260(10.43)	320(1.20x10 ⁴)
Ni(PyP) ₂	2.54	yellow	yellow	18,150(10.98) 11,070(9.40)	318(2.94x10 ⁴) 358(1.23x10 ⁴) sh

a. Abbreviations: Pald, pyrrole-2-aldehyde; PlP, 2,2'-(1'-pyrrolinyl)pyrrole; PyP, 2-(2-pyridyl)pyrrole

b. Moles of pyridine added per mole of solid complex

c. In pyridine solution

d. Molar extinction coefficient , e, in parentheses, are in l. mol⁻¹cm⁻¹; sh., shoulder

Proton Resonance Measurements.--All measurements were made at room temperature on a Varian A-60 spectrometer. Solutions were made with deuteriochloroform, and tetramethylsilane was used as an internal or external standard.

The spectrum of $\text{Ni}(\text{PlP})_2$, which has a solubility in deuteriochloroform of less than 0.5%, was obtained using a Varian C-1024 Time Averaging Computer coupled to the Varian A-60 mmr Spectrometer. The region between 325 and 385 cps was swept sixty times which increased the signal to noise ratio to about 5:1 from an original spectrum where no signal could be observed with a single sweep.

X-ray Powder Photographs.--Powder patterns were taken with a 57.3 mm Philips camera using copper radiation. The samples were mounted in 0.3 mm glass capillaries. The X-ray powder film numbers are: $\text{Zn}(\text{PyP})_2$, 2091; $\text{Cu}(\text{PyP})_2$, 2093; $\text{Ni}(\text{PyP})_2$, 2092 and 2099; $\text{Zn}(\text{PlP})_2$, 2094; $\text{Cu}(\text{PlP})_2$, 2095; and $\text{Ni}(\text{PlP})_2$, 2096.

Magnetic Measurements.--Magnetic measurements were performed at room temperature by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as a standard. The solid-state measurements were performed at 5.8 and 8.6 kgauss. The values reported are the averages of the values obtained at each field strength and are in Bohr Magnetons (BM), where $1 \text{ BM} = 0.927 \times 10^{-20} \text{ erg gauss}$.

Deviation of any value from the average value

reported in no case exceeds ± 0.05 BM. Diamagnetic corrections^{25,26} were applied to the complexes in calculating the magnetic moments. (See Table I for data and Appendix A for method of calculation.)

Thermogravimetric Analysis.--The thermogravimetric analysis (tga) of the Ni(PyP)_2 -pyridine adduct was done with a DuPont Model 900 Differential Thermal Analyzer coupled with a Model 950 Thermogravimetric Analyzer. A sample size of 10.18 mg and a programmed heating rate of $2^\circ/\text{min}$ were used. A faster heating rate of $5^\circ/\text{min}$ failed to produce a curve with distinct changes.

Molecular Weight Determination.--The molecular weight of Ni(PyP)_2 was determined in chloroform using a Mechrolab Model 301A Vapor Pressure Osmometer. The instrument had previously been calibrated with naphthalene in chloroform. Values obtained at nominal concentrations of 0.015 and 0.020 M agreed to within 1% of each other.

RESULTS AND DISCUSSION

The Copper Complexes.--The copper complexes Cu(Pald)_2 , Cu(PlP)_2 , and Cu(PyP)_2^* all have magnetic moments between 1.85 and 1.87 BM. The spin-only moment for one unpaired electron is 1.73 BM. The copper(II) complexes are d^9 which means that they have only one unpaired electron in the ground state. The increased magnetic moment of copper arises from what is known as 'temperature independent paramagnetism' or T.I.P.

T.I.P. is described in the quantum mechanical derivation of paramagnetic atomic susceptibility, as developed by Figgis, in the following manner.²⁷ If the difference in energy between the ground state level and the first excited state level is much greater than the thermal energy available (kT), then the excited levels cannot make a direct contribution to the susceptibility. As a consequence the first order coefficient in the expression for the atomic susceptibility is zero and the first order Zeeman effect which is proportional to $1/T$, the Curie law, is not observed. This has the effect of leaving an expression which is no longer temperature dependent and contains only the second order coefficient, the higher than second order coefficients having been assumed to be zero in the initial

* Anion abbreviations: Pald, pyrrole-2-aldehyde; PlP, 2,2'-(1'-pyrrolinyl)pyrrole; PyP, 2-(2-pyridyl)-pyrrole.

derivation.

The remaining second order coefficient may be considered as a magnetic-field induced mixing of the ground and excited state levels, or second order Zeeman effect, which lowers the energy of the ground state. The higher state being mixed may be a singlet or multiplet and can have an orbital magnetic moment different from that of the ground state. The measured magnetic moment is correspondingly increased or decreased with the extent of the interaction dependent on field strength and inversely proportional to the energy separation of the ground level and excited level. The effect is fairly common with ions of transition metal complexes and in addition to being designated as the second order Zeeman effect or temperature independent paramagnetism (T.I.P.) it has been called "Van Vleck high frequency paramagnetism." The effect is usually small compared to spin-only magnetic moments as in the present case with copper(II).

The ultraviolet-visible spectra, i.e. the ligand field region, of the three complexes are similar in that there is one broad band in this region. This appears at $15,870\text{ cm}^{-1}$ (molar extinction coefficient, ϵ , = 61) for Cu(Pald)_2 , $18,250\text{ cm}^{-1}$ (317) for Cu(PyP)_2 and $20,660\text{ cm}^{-1}$ (179) for the Cu(PlP)_2 . In each case the band is quite broad and tends to be distinctly asymmetric; it is most probably the result of two or more bands of fairly close energy.²⁸

Assignment of the ligand field bands of copper(II) complexes has proved to be most difficult and usually impossible.^{14,16,28} Consequently, the range in the energies of the bands among the complexes is not an indication of ligand strength or value of $10 Dq$, since the energies cannot be related to particular energy level transitions. However, the mere existence of the bands is an indication that the copper complexes are probably not regular tetrahedra. Lever²⁹ states that regular tetrahedral copper(II) is very uncommon due to the Jahn-Teller effect. Tetrahedral copper(II) complexes, if approximately regular, are expected to give a single broad band in the near-infrared ($\epsilon \approx 10^2$) and to have no absorption between 10,000 and 20,000 cm^{-1} . As distortion towards square planar increases, the bands in the near-infrared of tetrahedral copper(II) are expected to move towards higher frequency, *i.e.*, towards the previously transparent 10,000 to 20,000 cm^{-1} region.

In an attempt to determine more exactly the geometry of the copper complexes, X-ray powder photographs were examined for isomorphism. The nickel complexes prepared can be shown to be square-planar, and the zinc complexes are presumed to be tetrahedral. If one of the copper complexes could be shown to be isomorphous to either the zinc or nickel complex of the same ligand, its geometry would then have been established with good certainty. However, a lack of copper isomorphism with either the

zinc or nickel analog does not indicate that the copper complex is of some different geometry, only that it is of a different crystal structure.

In the two series $\text{Zn(PlP)}_2\text{-Cu(PlP)}_2\text{-Ni(PlP)}_2$ and $\text{Zn(PyP)}_2\text{-Cu(PyP)}_2\text{-Ni(PyP)}_2$, the copper X-ray powder photographs had no similarity to either their zinc or nickel analogs. Thus it could not be determined whether square-planar or tetrahedral geometry exists in the solid state for these copper complexes. The question of their geometry is left unresolved, since the determination would require a rather extensive X-ray crystallographic study.

For the above study the zinc complexes Zn(PlP)_2 and Zn(PyP)_2 were prepared without great difficulty. The preparation of Zn(Pald)_2 however, was attempted many times by several different methods without ever obtaining the complex. Ni(Pald)_2 also defied preparation even though an intensive effort was made to obtain this complex. Consequently an X-ray powder photograph of Cu(Pald)_2 was not taken since there are no analogs with which to make a comparison.

Pyridine adducts of copper complexes are quite common. Frequently copper(II) complexes will form one to one adducts, some of which have been shown to be square-pyramidal. Two to one complexes, which are distorted octahedra, are not uncommon. Occasionally, adduct formation has been used as evidence for determining the geometry of

the starting complex involved, but other evidence must be present since adduct behavior is far from conclusive.²⁰

For the three copper complexes prepared, three different classes of solid adduct formation are observed. Cu(Pald)_2 adds two moles of pyridine per mole of complex giving dark green crystals. Cu(PyP)_2 coordinates just one mole of pyridine per mole of complex, and Cu(PlP)_2 does not form a solid adduct at all. These results tempt one to speculate that perhaps Cu(Pald)_2 is either less sterically hindered or is closer to being truly square-planar than Cu(PyP)_2 and Cu(PlP)_2 , thus allowing it to take up more pyridine per molecule than the other complexes. While the steric hindrance conclusion can be supported to some degree with models, any conclusion as to the geometry must be foregone for lack of any other confirmatory evidence.

The interpretation of the ligand field spectra of copper(II) adducts has received attention recently; however, the ordering of the excited d levels appears to still be an open question.³⁰ Chakravorty and Kannan¹⁶ have in their work with the electronic spectra of pyrrole-2-alimine chelate copper(II) complexes reviewed the case for copper d^9 spectra. If a copper d^9 complex is tetragonal (D_{4h}), then three transitions are predicted for the one-hole d^9 configuration. However, if the bidentate ligands are not symmetrical then the symmetry becomes orthorhombic (D_{2h}) for the square-planar or distorted octrahedral complex.

In the latter case the degeneracy is removed and four transitions would be expected. These transitions are seldom well resolved, the usual case being where only one broad asymmetric band is observed. In spite of these difficulties, the spectra of pyridine adducts can sometimes be partially interpreted.³⁰

For four coordinate copper complexes it is not possible to predict accurately the number of expected bands since the complex may be square-planar, tetrahedral, or distorted. If in solution, however, two moles of pyridine are bonded to form the six coordinate complex then either D_{4h} or D_{2h} symmetry may be assumed, depending on the nature of the ligand system. This allows the examination of a spectrum with the expectation of finding a certain number of transitions and asymmetric bands may then be resolved into gaussian components. However, the resolution may be difficult and not unique, and the results are not always unambiguous.

In the present case all the copper complexes form adducts when dissolved in pyridine, as evidenced by the change in the color and spectrum of each. Except for $Cu(PyP)_2$, which has three distinct bands, the complexes show the usual single broad asymmetric band in the ligand field region.

Although the complexes distinctly form adducts in pyridine solution, these do not necessarily have the same

pyridine ratio as the solid adducts formed. This is obvious in the case of Cu(PlP)_2 which forms no solid adduct at all, but changes color in pyridine solution. The determination of the relative stability constants for the pyridine adducts of the complexes would determine the number of pyridines coordinated. The spectra obtained could then be treated by the methods of Funck and Ortolano.³⁰ Their treatment consists of fitting curves by trial and error to the observed spectral shapes. This type of investigation would be an excellent problem for an instrument such as the DuPont Model 310 Curve Resolver.

For a study such as the above, the Cu(PyP)_2 adduct could prove to be especially valuable since even without curve fitting techniques three bands can be distinguished, in contrast to the usual case where only one asymmetric peak is observed. It would not be improbable that such efforts with these complexes could help significantly in the assignment of copper(II) ligand field spectra. Because of the complexity of copper(II), much work remains to be done in interpreting its spectra.

The Nickel Complexes. -- Two nickel complexes were prepared and studied, Ni(PlP)_2 and Ni(PyP)_2 . As previously mentioned, the third complex, Ni(Pald)_2 defied successful preparation despite an intensive effort. Attempts using all the procedures found successful for the other complexes, which are described in the experimental section, were made

for the nickel-Pald system. Additionally a number of other methods of complex formation which have been reported in the literature were tried. In no case did any of the efforts meet with success. Logic would seem to dictate that the nickel(II) complex can be prepared since the copper analog can be prepared with little difficulty. Logic notwithstanding, Ni(Pald)_2 has not yet been prepared.

The nickel complexes have solid state magnetic moments of 0.45 to 0.46 BM indicating that they are diamagnetic. Proton resonance measurements show conclusively that the complexes are also diamagnetic in deuteriochloroform solution since the contact shifts expected for paramagnetic nickel(II) are absent.¹⁴ The fact that the d^8 nickel complexes are diamagnetic indicates that the complexes are square-planar.³¹ Other nickel(II) geometries do not result in diamagnetic complexes.

Square-planar nickel(II) complexes can be expected to show absorption in the region of 20,000 to 22,000 cm^{-1} due to the $^1A_{1g} \rightarrow ^1A_{2g}$ transition. Other transitions appear at higher energies.³²⁻³⁴ The validity of this assignment is not, however, accepted by all authors. Lever³⁵ feels that it is not possible to make definite assignments for square-planar nickel(II) complexes since a systematic interpretation of the spectra is not feasible. Nevertheless, such an assignment is a fairly common practice, accepted by many, and will be used here.

The Ni(PlP)_2 complex has a fairly broad band at $21,050 \text{ cm}^{-1}$ (169) that appears as a shoulder on the side of the far more intense charge transfer bands, which have maxima at $24,630 \text{ cm}^{-1}$ and higher energies. The $21,050 \text{ cm}^{-1}$ band is assigned as the $^1A_{1g} \rightarrow ^1A_{2g}$ transition. The frequency and molar extinction coefficient are in good agreement with previous studies of neutral square-planar nickel(II) complexes;^{14,19,33,34,36} however, the assignment is at odds with earlier work.^{19,37}

In the ultraviolet-visible spectrum of Ni(PyP)_2 there is observed no spectral band that can be attributed to $\underline{d} \rightarrow \underline{d}$ transitions. This is almost certainly due to the fact that the low energy tail of the charge transfer bands at $25,450 \text{ cm}^{-1}$ and $27,170 \text{ cm}^{-1}$ is still quite intense throughout the visible range. For instance, at $16,500 \text{ cm}^{-1}$ the molar extinction coefficient, ϵ , is greater than 200. This is well beyond the area where the $^1A_{1g} \rightarrow ^1A_{2g}$ transition for a square-planar nickel(II) complex is expected to occur.³²⁻³⁴

Gray and Ballhausen have also assigned ligand-metal charge transfer bands for the square-planar nickel(II) complex $\text{K}_2\text{Ni(CN)}_4 \cdot \text{H}_2\text{O}$.³² This is not attempted for the Ni(PyP)_2 or Ni(PlP)_2 complexes due to the greater complexity of their spectra.

When bivalent nickel is in an octahedral or pseudo-octahedral configuration, three spin-allowed transitions from the $^3A_{2g}$ ground term to the three excited triplet terms

are expected. They are ${}^3A_{2g} \rightarrow {}^2T_{2g}$ from 7,000 to 13,000 cm^{-1} , ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ from 11,000 to 20,000 cm^{-1} , and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ from 19,000 to 27,000 cm^{-1} .³⁸ All three transitions typically have low molar extinction coefficients (ca. $\epsilon = 2-20$). The last transition occurs where charge transfer bands are usually intense and consequently, in a ligand system where charge transfer absorption is present, the ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ transition usually will not be observed. The ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition is also equal to $10 Dq$.

The advantages of the octahedral system were utilized by dissolving the nickel complexes in pyridine. The resulting pale yellow solutions can be assumed to be caused by the pseudo-octahedral system of the original square-planar complex coordinating two pyridines. This assumption is supported by the ligand field spectra of the complexes. Each complex has only two low-intensity bands beyond the ultraviolet region charge transfer bands. Ni(PyP)_2 in pyridine has broad bands at 11,070 cm^{-1} (9.40) and 18,150 cm^{-1} (10.98) while Ni(PlP)_2 has broad bands at 10,260 cm^{-1} (9.24) and 17,950 cm^{-1} (10.43). The lower frequency bands are assigned as ${}^3A_{2g} \rightarrow {}^3T_{2g}$, and the higher frequency bands are assigned as ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$. In neither case are the bands observed to be split, which is not unusual for symmetries that are less than octahedral, i.e., O_h . Cases that are tetragonal (D_{4h}) or orthorhombic

(D_{2h}) usually show splitting only of the ${}^3A_{2g} \rightarrow {}^3T_{2g}(P)$ band, which here is obscured by the presence of intense charge transfer bands. This precludes the calculation of in-plane and out-of-plane values of Dq , which would be possible if the split band could be observed.³⁹

As was previously mentioned, the ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition is equal to $10 Dq$. Consequently, Dq for $Ni(PyP)_2$ in pyridine is equal to 1107 cm^{-1} , and for $Ni(PlP)_2$ in pyridine Dq is equal to 1026 cm^{-1} . This value is for an octahedral nickel(II) complex, which the nickel complexes in solution approximate. Using the rule of 'average environment' as developed by Figgis,⁴⁰ the value of Dq of the ligands may be found. The rule states that for a set of mixed ligands the value of Dq is the result of the weighted average of the value of Dq associated with each of the complete sets of ligands separately. Assuming that the experimental value of Dq is due to the square-planar complexes with two molecules of pyridine coordinated, a Dq value for the PyP and PlP ligands can be calculated. With the experimental value of Dq equal to $1,000 \text{ cm}^{-1}$ found by Rowley and Drago⁴¹ for pyridine in the complex $Ni(Pyridine)_6^{++}$, the value of Dq for the PyP ligand is equal to 1160 cm^{-1} , and for PlP Dq is equal to 1039 cm^{-1} . Strictly speaking, these values of Dq are for six coordinated nickel(II) complexes.

The Racah parameter, B, also called the interelectronic repulsion parameter, is often of theoretical interest. For octahedral nickel(II) it is found from the relation:

$$\frac{{}^3A_{2g} \rightarrow {}^3T_{1g}}{{}^3A_{2g} \rightarrow {}^3T_{2g}} \propto \frac{Dq}{B}$$

The proportionality may be interpreted from the Tanabe-Sugano diagram⁴² or found directly from tables which have been prepared.⁴³

The attempt to find B for the pyridine adducts of the nickel complexes led to unrealistic values that were greater than the value of Dq. This result is most likely due to the fact that a small change in the ratio of the two bands produces a large change in Dq/B. This is coupled with one or more of the following approximations. First, the assignment of the energy of the spectral bands is less exact than would be desirable. The bands are quite broad and of low intensity so that the assignment could perhaps be in error by as much as 300 cm⁻¹. Also the lower frequency band is the broader of the bands in both cases, giving rise to a like uncertainty for Dq. Secondly, in the present case we are dealing with a mixed ligand system, one in which the geometry is less than octahedral. Even a fairly small difference in the estimated energy of one band would result in considerable error in the calculation of B.

In an atmosphere of pyridine, the nickel complexes form solid adducts. The Ni(PlP)_2 reversibly coordinates two molecules of pyridine to form the 2:1 complex that is expected. Ni(PyP)_2 appears to reversibly coordinate 2.5 molecules of pyridine. Again, a 2:1 complex was expected, and the addition of an extra half mole of pyridine is difficult to interpret. The solution work described above makes clear that when Ni(PyP)_2 is dissolved in pyridine a six coordinated nickel(II) complex is observed.

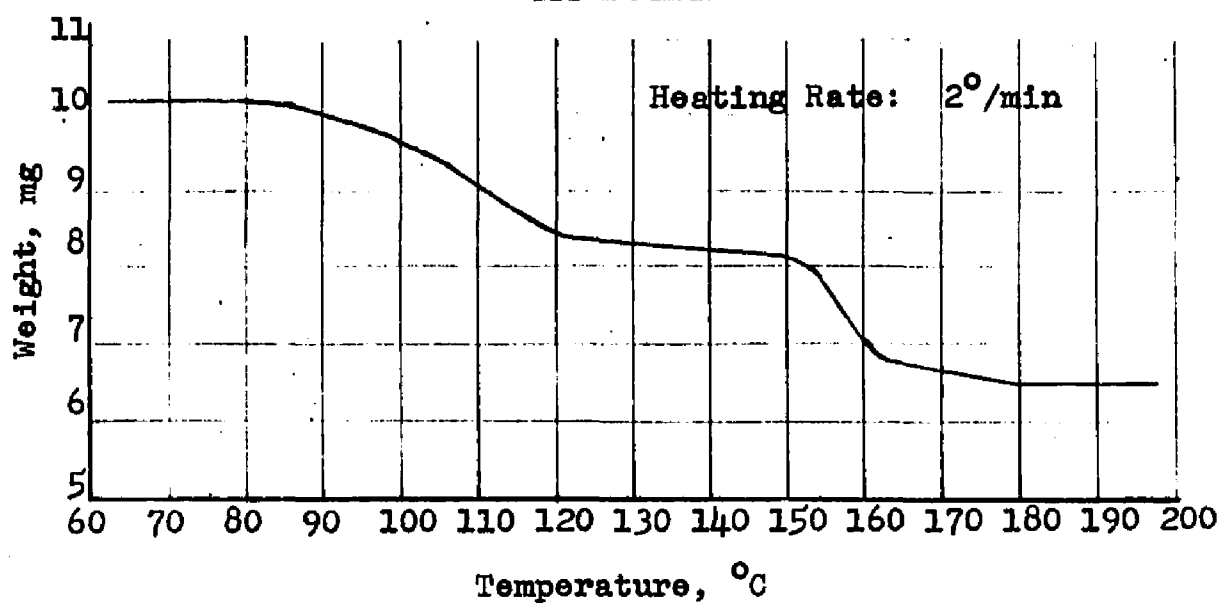
There are at least three ways in which an extra one-half mole of pyridine might be absorbed. The first is that the nickel in some way actually manages to coordinate and hold more than two moles of pyridine, giving $\text{Ni(PyP)}_2(\text{Py})_{2.5}$. Secondly, the extra pyridine could be pyridine of crystallization and not complexed, but held in the crystal structure giving $[\text{Ni(PyP)}_2(\text{Py})_2] \cdot \frac{1}{2}\text{Py}$. Or the pyridine might be reacting with the ligand to form some new organic compound. This latter possibility is rejected on the basis that all the pyridine is held reversibly and when removed in a vacuum desiccator leaves the original Ni(PyP)_2 complex unaltered.

In an attempt to distinguish between the first two possibilities, the infrared spectrum of the adduct was examined. Pyridine has bands near 400 and 600 cm^{-1} that are shifted upon complexation.⁴⁴ Examination of the spectrum showed that complexed pyridine is definitely present, while it is uncertain as to whether uncomplexed pyridine is present

or not. The uncertainty arises from the fact that the spectrum in this region is very complex due to the ligand, half of which is the pyridine molecule. The infrared can only be regarded as inconclusive.

To further characterize the unusual adduct, a thermogravimetric analysis (tga) was run (See Table IV and Figure II). From the results it appears that one mole of pyridine is lost, then a second mole, and lastly just prior to melting, the half mole of pyridine is lost. This is contrary to what would have been expected for pyridine of crystallization. Thus it may be concluded from this data that the peculiar extra half mole of pyridine is more than pyridine of crystallization and is held by the nickel(II) in some fashion.

As an additional piece of information, a molecular weight determination of the adduct would be of interest. For a solution method this would have to be carried out in pyridine since, if the solid adduct is dissolved in any other solvent, the color of the original complex is obtained unless excess pyridine is added. A molecular weight in pyridine could not be obtained. However, a molecular weight of the original Ni(PyP)_2 complex was obtained in chloroform. This was sought mainly to determine if the original complex was a polymer or a monomer. A value of 290 was found, compared to the calculated value of 345. It is concluded that the complex in solution is monomeric despite the large

Figure IITga Curve of the Solid Ni(PyP)_2 -Pyridine Adduct^aTable IVTga Data for the Solid Ni(PyP)_2 -Pyridine Adduct^a

<u>Temperature Range(°C)</u>	<u>Weight loss (mg)</u>	<u>% Weight loss</u>	<u>Moles of, Pyridine^b</u>
80 - 118	1.62	15.9	1.10
118 - 160	1.54	15.0	1.03
160 - 179	0.49	4.8	0.33

 Total 2.46

a. Anion abbreviation; PyP, 2-(2-pyridyl)pyrrole

b. Based on a pyridine to complex ratio of 2.5:1

difference between the calculated and found values. It must again be emphasized that the behavior in solution is not necessarily the same as the behavior observed for the solid. Obviously, the crystal structure of the Ni(PyP)_2 -pyridine adduct would be of considerable interest, but is beyond the scope of the present investigation.

The Cobalt Complexes.--The cobalt(III) complexes Co(Pald)_3 and Co(PyP)_3 were prepared and studied. As a starting material for their preparation a divalent cobalt source was oxidized, resulting in the formation of the cobalt(III) complex. The requirement that the metal must be oxidized, and the fact that cobalt(III) reacts slowly, necessitates longer reaction times than needed for the previously described complexes.

The preparation of the cobalt(II) complexes was attempted by protecting the reaction from air with an atmosphere of nitrogen. These efforts still yielded only the cobalt(III) product. This result may have been due to traces of oxygen in the reaction, or more likely to the reduction of some of the hydrogen ion that is released from the pyrrole when it becomes anionic. The reduction of hydrogen ion and the release of hydrogen gas by the oxidation of a metal has been observed for similar reactions.⁷

A number of attempts to prepare the Co(PlP)_3 complex were made. A variety of products were obtained and analyzed. The analytical results usually fell between the calculated

percentages for Co(PlP)_2 and Co(PlP)_3 . Repeated recrystallizations from a wide variety of solvents did not yield any product whose analysis was satisfactory for either oxidation state. The analytical results seemed to indicate a mixture of the cobalt(II) and cobalt(III) complexes; however, ultra-violet-visible spectra did not confirm the presence of cobalt(II), and indicated only that a cobalt(III) complex was present.^{14,15}

One other possibility is that a polymeric product was formed. This could well account for the fact that while handling various reaction products in solution and while attempting recrystallizations, fractions were obtained which could not be redissolved. These fractions did not, however, have consistent analyses. Attempts to aid the oxidation of cobalt(II) to cobalt(III) with hydrogen peroxide or other oxidants were totally unsuccessful. In spite of many unsuccessful efforts, the preparation of Co(PlP)_3 should be possible.

Complexes of cobalt(III) are expected to be diamagnetic having magnetic moments of about 0.5 BM. The fairly large moment is principally due to the second order Zeeman effect with higher ligand field terms which causes temperature independent paramagnetism (T.I.P.).⁴⁵ This is the same effect that increases the magnetic moment of the copper(II) complexes above the spin-only value and was reviewed in the discussion of the copper complexes. The moment of Co(Pald)_3

is 0.44 BM; for Co(PyP)_3 the moment is 0.56 BM. No significance can be attached to the small difference in magnetic moments of the two complexes.

Octahedral, O_h , cobalt(III) complexes have a ligand field spectrum consisting of two bands. At about $20,000 \text{ cm}^{-1}$ there is a band assigned to the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition, and at about $30,000 \text{ cm}^{-1}$ a band that is assigned as ${}^1A_{1g} \rightarrow {}^1T_{2g}$.⁴⁶ For complexes of organic ligands that have strong ultra-violet components, the band at $30,000 \text{ cm}^{-1}$ is usually obscured, making the determination of $10 Dq$ impossible. In the present case even the band at $20,000 \text{ cm}^{-1}$ is obscured for Co(PyP)_3 , since the low energy tail of the intense ultra-violet band at $26,670 \text{ cm}^{-1}$ extends out into the visible so far that at $18,200 \text{ cm}^{-1}$ the molar extinction coefficient is still greater than 100. Co(Pald)_3 has a broad band at $15,870 \text{ cm}^{-1}$ (61) which can be assigned as the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ transition.⁴⁶

When the two coordinating sites of a bidentate ligand are different, the ligand is of a type known as AB. Both the Pald and PyP ligands fall into this category. Octahedral complexes of AB type bidentate ligands can be in either a cis or trans configuration. This is to say that if one takes the proper three-fold axis of an octahedron, for the cis case all the 'A' groups of the three bidentate ligands are on the near triangular face and all the 'B' groups are on the further triangular face. The octahedron

thus has three-fold rotational symmetry. If, on the other hand, one of the ligands is reversed, then there are two 'A' groups and one 'B' group on the near triangular face and the three-fold symmetry is lost. This lack of symmetry is also the case for all of the other axes so that, in fact, the octahedron contains no symmetry elements.

To distinguish cis and trans isomers of octahedra formed with bidentate ligands, proton magnetic resonance can be applied. For the unsymmetrical trans isomer a given substituent on each chelate ring could, in principle, produce a separate resonance, but only a single resonance for the same substituent should occur in the cis form. This behavior has been observed for a number of trivalent complexes including cobalt(III).^{13,17} In the cases reported for cobalt(III) the configurations have been found to be trans and one or more substituent resonances in the mmr spectrum have been split into three components. It is not necessarily true that a lack of splitting in the peaks of a substituent is evidence of a cis isomer. It would be possible that protons of a substituent of a trans complex could be chemically so similar that they would not give rise to any splitting. Thus it is not safe to assume that lack of splitting is proof of a cis configuration without other confirmatory evidence.

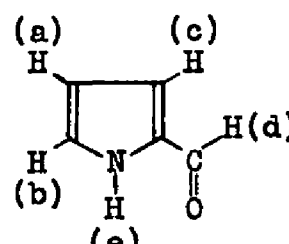
Proton resonance spectra were examined for the two cobalt complexes and their free ligands in d-chloroform

solution. The spectrum of HPyP is unusually complex, each hydrogen signal being split into more than a half dozen closely spaced peaks. None of the resonances gives anything near a sharp singlet, nor even a recognizable pattern. In the complex the situation is somewhat worse, in that the concentration is not as high and consequently the noise level is increased. In addition, the previously separated peak areas merge, making assignment of the pattern impossible. As a result, if splitting does occur it remains undetected and the configuration of Co(PyP)_3 remains unknown.

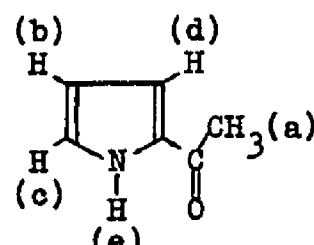
The Co(Pald)_3 complex represents a far more interesting case. The mmr spectrum of the H-Pald ligand with assignments is given in Table V. These assignments are in agreement with the literature.⁴⁷ The actual spectrum of the Co(Pald)_3 complex is presented in Figure III. The spectrum of the complex is not so readily assigned as that of the ligand. The broad hump at 7.9 to 8.4 ppm looks much like a proton on a nitrogen, but if this is so, then a totally different bonding scheme must be developed.

Before the cis-trans configuration of Co(Pald)_3 can be examined, the assignment of the spectrum of the complex must be made. To clarify the problem, the cobalt(III) complex of 2-acetylpyrrole (HActP) was prepared. This is HPald where the aldehyde hydrogen has been replaced by a methyl group. The spectrum of the HActP ligand with assignments is given in Table V and the actual spectrum of the Co(ActP)_3 complex

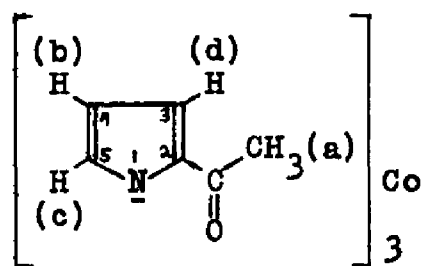
Table VNmr Assignments of H-Pald, HActP and Co(ActP)₃

	<u>Position</u>	<u>Peak (ppm)</u>
	a	6.30
	b	6.98
	c	7.17
	d	9.45
	e	Ca 11.08

Pyrrole-2-aldehyde

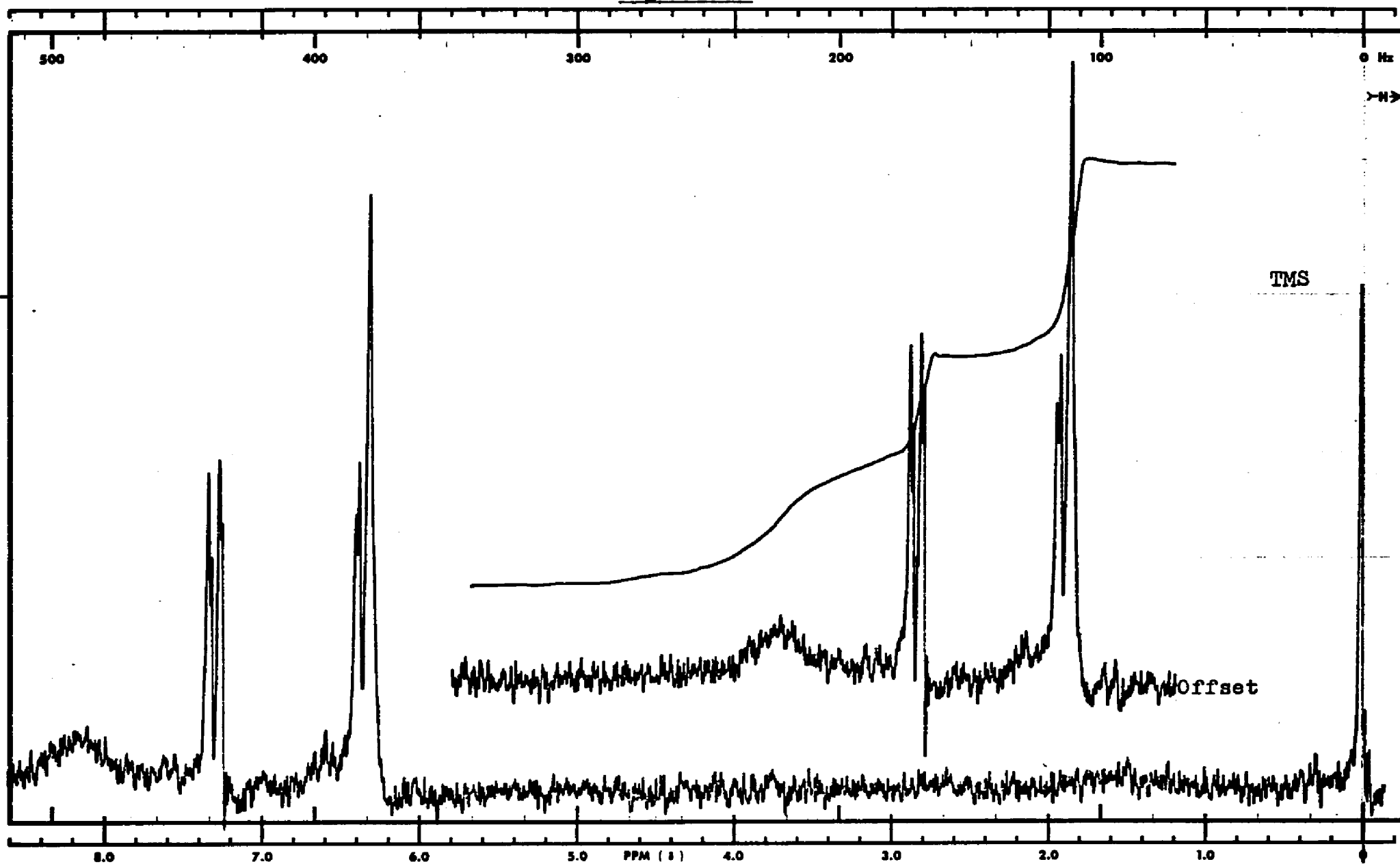
	<u>Position</u>	<u>Peak(ppm)</u>
	a	2.44
	b	6.27
	c	6.95
	d	7.10
	e	Ca 10.98

2-Acetylpyrrole

	<u>Position</u>	<u>Peak(ppm)</u>
	a	2.51
	bc	6.21
	d	7.18

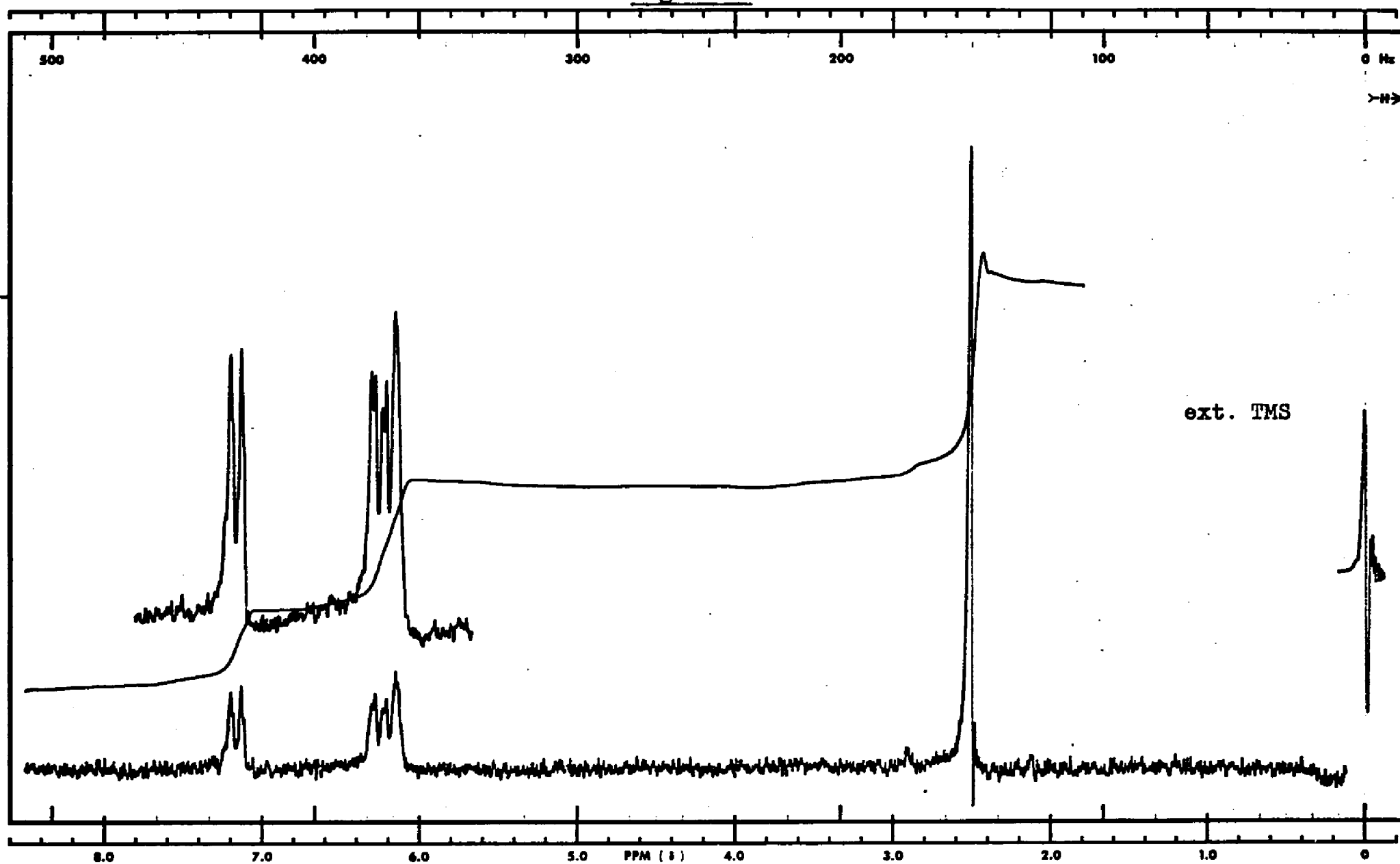
Co(ActP)₃

Figure III



The Nmr Spectrum of the Cobalt(III) Complex of Pyrrol-2-aldehyde, Co(Pald)_3

Figure IV



The Nmr Spectrum of the Cobalt(III) Complex of 2-Acetylpyrrole, Co(ActP)_3

is presented in Figure IV. The assignment of this spectrum is fairly straightforward and is given in Table V based on the following considerations. The single proton at 7.18 ppm is the region of the 3- and 5-position protons before complexation. The 5-position proton is next to the coordinated nitrogen site, thus the signal at 7.18 ppm is assigned as the 3-position proton, the site least affected by coordination. The 4- and 5-position protons appear to have similar chemical shifts and are assigned as causing the distorted triplet in the 6.21 ppm region. This assignment appears to be unambiguous.

On comparison of the $\text{Co}(\text{ActP})_3$ and the $\text{Co}(\text{Pald})_3$ spectra, the notable and obvious similarity is that the appearance of the pyrrole resonances of $\text{Co}(\text{ActP})_3$ are much like the peaks at 7.31 and 6.36 ppm of $\text{Co}(\text{Pald})_3$, indicating that these three protons are respectively the 3- and 4,5-position protons of the pyrrole ring of Pald. This leaves unassigned the very broad hump at 7.9 to 8.4 ppm. Additionally, the aldehyde proton has not been assigned. The aldehyde proton would not be expected to be as broad as the hump at 7.9 to 8.4 ppm; however, a N-pyrrole hydrogen is not expected to be present either.

A proton attached to a nitrogen atom such as in pyrrole would be expected to exchange rather rapidly with D_2O , especially if a drop of acid were added. An aldehyde proton would not be expected to exchange at all. To dis-

tinguish definitely the type of hydrogen represented by the broad resonance at 7.9 to 8.4 ppm in the Co(Pald)_3 spectrum, the solution was shaken with a drop of D_2O and the region from 9.0 to 7.0 ppm was scanned. A drop of hydrochloric acid was added and the mixture was shaken again. No change in the broad hump or its integration was apparent even after the D_2O -acid solution was heated and shaken for thirty minutes. From these observations and from comparison with the spectrum of Co(ActP)_3 , it is concluded that the broad hump at 7.9 to 8.4 ppm is indeed due to the aldehyde proton of Pald. Additionally, the infrared spectrum of Co(Pald)_3 shows no trace of the N-H stretch which is characteristic in the free ligand.

In considering the cis-trans nature of Co(Pald)_3 , it has already been noted that if Co(Pald)_3 were trans, then the aldehyde proton could give rise to three slightly different signals. If the three signals were not resolved, a broadened peak could result. This would not, however, be expected to produce a very broad hump some 0.5 ppm wide. Instead, a peak with a half-height width twice or perhaps even three times as great as the ligand's original peak might be expected. Thus it is concluded that the response at 7.9 to 8.4 ppm in the spectrum of Co(Pald)_3 is not due to a trans effect, but to some other factor.

Also, none of the other peaks in the Co(Pald)_3 spectrum shows the type of splitting that could be attributed

to the trans form. The same is true for $\text{Co}(\text{ActP})_3$ where the methyl peak is very sharp without any observed splitting. The lack of splitting is not necessarily due to the cis configuration. Splitting could be absent in the trans if all the protons are free from intermolecular interactions. From examining models of trans- $\text{Co}(\text{Pald})_3$ and trans- $\text{Co}(\text{ActP})_3$, it appears that there should be very little steric interaction between any proton and another ligand molecule. Consequently, the lack of splitting cannot be assumed to arise from the symmetrical cis configuration, since it would be not unlikely for the trans case as well. Thus the configuration of neither complex has been resolved.

Other mechanisms that may produce line broadening generally fall into the categories of 'spin-spin' interactions and 'spin-lattice' interactions. Spin-spin interaction arises when the nuclear magnetic moment of a proton comes into resonance with a neighboring proton's moment. When two moments become resonant they may exchange their spins. As a result a proton under investigation may, if conditions are right, have an alternate way of relaxation from its excited state. If the exchange is efficient (i.e., fast), the observed line width will be broadened. One strict criterion for the existence of such a mechanism is that the exchanging hydrogen nuclei must be physically close to each other.⁴⁸ This consideration rules out spin-spin exchange for the aldehyde proton of $\text{Co}(\text{Pald})_3$. Models

clearly show that these protons are well separated from any other proton in the complex for both cis and trans configurations. Additionally, the extreme broadening observed is not characteristic of a spin-spin interaction.

Spin-lattice interactions are of two basic types; paramagnetic broadening and nuclear quadrupole moment broadening.⁴⁹ The latter is effective only when the proton is bonded to an atom that has a nuclear spin, I , greater than $\frac{1}{2}$. While it is true that cobalt 59 (natural cobalt) has a spin equal to $7/2$, the cobalt nuclear moment cannot be expected to interact with the aldehyde proton through the carbonyl group that separates them.

The second type of spin-lattice broadening, paramagnetic broadening, occurs when a paramagnetic species is present. An electron magnetic moment is some three orders of magnitude greater than a nuclear magnetic moment. Consequently, the motion of a paramagnetic species in the lattice (here this would be the liquid solution) can produce an intense fluctuating local field which will greatly reduce spin-lattice relaxation times. The reduction of the lifetime of the excited state makes the energy uncertain and gives rise to a broadened response.

Cobalt(III) was shown earlier to have a small magnetic moment due largely to temperature independent paramagnetism. It seems probable in view of the preceding discussion of line broadening processes that the aldehyde

proton of Co(Pald)_3 is made into a broad hump by this paramagnetic interaction mechanism. Just as paramagnetic coupling does not shift the positions of peaks uniformly, neither must paramagnetic broadening be equal for all protons. Thus the pyrrole protons are not broadened.

The selection of the paramagnetic effect for the mechanism of the observed spectra is more by a process of elimination rather than one of choosing a mechanism that is particularly suitable. Paramagnetic broadening is not unlikely, since the broadening cannot be shown to arise from one of the other mechanisms. The evidence in support of the suggested cause of the aldehyde broadening is not conclusive and the influences affecting the nmr spectrum of Co(Pald)_3 are certainly deserving of more intensive study in the future.

The Iron Complex.--The only iron complex prepared and studied was the iron(III) complex of HPyP. Preliminary efforts to prepare the iron complex of either HPald or HPLP were unsuccessful. With both systems only dark tarry residues were obtained using the methods found successful for the other complexes. The attempted syntheses were not intensively pursued, since for iron(III) complexes the physical properties that were to be investigated do not lend themselves to very much significant interpretation.

The Fe(PyP)_3 complex exhibits a magnetic moment of 2.26 BM at two different field strengths at room temperature.

The moment indicates one unpaired electron for the d^5 iron(III), or a t_{2g}^5 configuration. The ground state is then ${}^2T_{2g}$.⁵⁰ The value of the magnetic moment is larger than the spin-only value of 1.73 BM for one unpaired electron due to the considerable amount of orbital contribution. The orbital contribution for the low-spin t_{2g}^5 configuration of iron usually gives rise to moments of ~ 2.3 BM.⁵¹

The orbital contribution to the magnetic moment is not the second-order Zeeman (or temperature independent paramagnetic) effect discussed previously. It is a direct coupling of the ground state spin angular momentum and orbital angular momentum. The orbital angular momentum contributes fractionally resulting in a susceptibility that is some fraction greater than the spin-only value. It can be shown that the orbital angular momentum is zero for A and E ground terms, but that it may exist for T ground terms.^{31,52} Low-spin iron(III) has a T_{2g} ground term, and it is this effect that increases its magnetic moment. Unfortunately, a more complete description becomes very complex, involving a considerable amount of group theory, and is not readily discussed in general terms.

That the iron(III) is in a low-spin (t_{2g}^5) state is an indication of the strength of the 2-(2-pyridyl)pyrrole ligand. Only the strongest ligands such as cyanide, dipyridine and 1,10-phenanthroline will produce low-spin iron(III)

complexes.⁵¹ From the structure of 2-(2-pyridyl)pyrrole one would predict that it would fall into the class of strongfield ligands for iron(III).

In solution the $\text{Fe}(\text{PyPy})_3$ complex is an intense purple. Strong charge transfer bands in the ultraviolet extend well into the visible region, and an intense band at $18,870 \text{ cm}^{-1}$ (3010) nearly in the middle of the visible region is probably also a charge transfer absorption. A broad shoulder that extends from $15,625 \text{ cm}^{-1}$ to $13,160 \text{ cm}^{-1}$ (~ 400) is likely due to ligand field interactions and almost certainly represents more than one transition. Interpretation of the ligand field bands even for the related and well-studied complex $\text{K}_3\text{Fe}(\text{CN})_6$ is very uncertain;⁵⁰ therefore, no attempt is made to assign the ligand field spectrum of the $\text{Fe}(\text{PyP})_3$ complex.

The use of nmr to investigate the cis-trans character of an octahedral iron(III) complex cannot be expected to be productive. Iron(III) is paramagnetic and will as a consequence radically shift the proton resonances from their free ligand positions. Shifts up to $10,000 \text{ cps}$ would not be unexpected. Additionally, as pointed out for $\text{Co}(\text{PyP})_3$, the spectrum of HPyP is very complex with a great deal of fine structure. The existence of so much fine structure for the free ligand makes the observation of any additional splitting extremely difficult. Thus, even if an nmr spectrum could be obtained, it is doubtful that it could be interpreted with

regard to the cis-trans configuration of the complex.

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APPENDIX A

Magnetic Measurements.--To determine the magnetic moments of the complexes studied, the following measurements were made using the Gouy method.²⁵

$W_{T,NF}$	Weight of the tube empty, field off
$W_{T,F}$	Weight of the tube empty, field on
$W_{TS,NF}$	Weight of the tube and sample, field off
$W_{TS,F}$	Weight of the tube and sample, field on

The same measurements were made for the standard mercury(II) tetrathiocyanatocobaltate(II). The tube constant R, a measure of the field strength and tube characteristics, can be calculated from equation (1). The

$$R = \frac{(X_{MS})(W_S)}{(\Delta W_S)(T)} \quad (1)$$

symbols used in equation I have the following meaning.

X_{MS} = Molar susceptibility of the sample (in this case the standard for which $X_M = 4820 \times 10^{-6}$ cgs units)

$W_S = W_{TS,NF} - W_{T,NF}$

$\Delta W_S = (W_{TS,F} - W_{T,F}) - W_S$

T = Temperature in °K

The molar susceptibility of the complex is then

found from the relation shown in equation (2). MW_S is

$$X_{MS} = R \frac{(\Delta W_S)}{W_S} (MW_S) \quad (2)$$

the molecular of the sample and ΔW_S and W_S are determined in the same manner as was done for the standard.

The value of X_{MS} found must be corrected for the diamagnetic contribution of the ligands and the closed shells of the metal ions. Additive element corrections²⁵ and experimental values²⁶ were combined to determine values for the ligands 2-(2-pyridyl)pyrrole, 2,2'-(1'-pyrrolinyl)-pyrrole, and pyrrole-2-aldehyde of -88.0, -87.7* and -49.0 (all are $\times 10^{-6}$) respectively. The value of -12.8($\times 10^{-6}$) was used to correct for the inner electron shells of each of the metal ions. Thus the correction for $Cu(PyP)_2$ is shown as an example in equation (3).

$$(-12.8) + 2(-88.0) = -188.8 \times 10^{-6} = X_M \text{ dia corr} \quad (3)$$

The corrected susceptibility of the metal is found from the relation shown in equation (4).

* Since in this ligand the C=N of 1-pyrrolinyl is conjugated with the pyrrole part of the ligand, the constitutive correction for one conjugated carbon is used rather than the correction for a C=N-R group, in line with the corrections applicable to the calculation for pyrrole and pyridine.

$$\chi_{MS} = \chi_{M \text{ metal}} + \chi_{M \text{ dia corr}} \quad (4)$$

Using the corrected unsuceptibility $\chi_{M \text{ metal}}$, usually called $\chi_{M \text{ corr}}$, the magnetic moment μ_{eff} in BM is found from equation (5).

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_{m \text{ corr}}} \quad (5)$$